

Original Paper

The Influence of Climate Conditions on Weighing Results

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Abstract. The influence of atmospheric pressure, air temperature, and relative air humidity on weighing results was determined in a long-term experiment. Two magnesium and three aluminium cylinders were weighed in a room without air conditioning over a period of more than three months. The climate parameters were automatically registered every 10 minutes. The climate data allow to calculate the masses from the weighing values which are subject to air buoyancy. It is then possible to check the validity of the empirical Schwartz equation for the calculation of the air density. The match between theory and experimental results is excellent for the influence of pressure and temperature and is weaker for the influence of humidity. The influence of this latter parameter on weight values is rather low and may be corrupted by water adsorption effects on the surfaces. It was found that the climate parameters can be looked at as triangular distributions rather than the previously proposed rectangular ones for the calculation of the weighing uncertainty budget.

Key words: Mass determination; weighing; measurement uncertainty; climate influence.

Measurement data in physics and chemistry should come along with their uncertainty [1]. Weighing

operations can be accomplished at a relative uncertainty in the 10^{-5} range with regard to the technical performance of the balance but the buoyancy effect is in the 10^{-3} range for objects with density around 1000 kg m^{-3} [2]. The uncertainty of buoyancy can easily dominate the uncertainty of a mass determination. Therefore it is wrong to display the uncertainty of a weighing operation by the technical data of the balance alone. Buoyancy and its cause, the air density, depend on the climate parameters atmospheric pressure, air temperature, and air humidity [3]; as a consequence, the uncertainty of the buoyancy depends on the uncertainty of the climate data [2].

With this study we intend to demonstrate the validity of the theoretical concepts of air buoyancy in the context of electronic laboratory balances by experimental data. It is of fundamental nature and has little consequences for, e.g., a typical gravimetric analysis (and none for a typical HPLC analysis of an environmental sample). Yet analysts involved in highly resolved weighing operations (resolution in the 10^{-4} range or better) should be aware of the climatic influences on their work.

Physical and Mathematical Background

Weighing with today's electronic laboratory balances is based on the comparison of the masses of the object

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to be weighed and a built-in reference weight. Both the object and the reference are subject to air buoyancy but due to the comparison there is no apparent deviation between observed weighing value (the value shown on the balance display) and mass if the object has the same density as the reference weight, namely 8006 kg m^{-3} (steel). However, in most weighing situations the object has a lower density, and its weighing value w_o is lower than its mass m_o . The relevant relationship is as follows [2, 4]:

$$m_o = w_o \frac{1 - (\rho_a/\rho_r)}{1 - (\rho_a/\rho_o)} = w_o \frac{\rho_o(\rho_r - \rho_a)}{\rho_r(\rho_o - \rho_a)} \quad (1)$$

where ρ_a , ρ_r and ρ_o are the densities of air, reference weight and the weighed object, respectively. The inverse function is obvious:

$$w_o = m_o \frac{\rho_r(\rho_o - \rho_a)}{\rho_o(\rho_r - \rho_a)} \quad (2)$$

The air density in kg m^{-3} can be approximated by an empirical equation [3]:

$$\rho_a = \frac{A \cdot p - B \cdot h_r \cdot \exp(C \cdot t)}{273.15 + t} \quad (3)$$

where p = atmospheric pressure in Pa (or $\text{kg m}^{-1} \text{ s}^{-2}$), h_r = relative air humidity in %, t = air temperature in $^{\circ}\text{C}$, $A = 0.0034848$, $B = 0.009024$, and $C = 0.0612$. The equation is valid for ambient conditions ($90,000 \text{ Pa} \leq p \leq 110,000 \text{ Pa}$, $10^{\circ}\text{C} \leq t \leq 30^{\circ}\text{C}$, $h_r \leq 80\%$) with a deviation of less than 10^{-4} . It yields an air density at $100,000 \text{ Pa}$, 20°C and 40% of 1.1846 kg m^{-3} .

The influence of air density on the weighing value is described by the partial derivative of Eq. (2):

$$\frac{\partial w_o}{\partial \rho_a} = m_o \frac{\rho_r(\rho_o - \rho_r)}{\rho_o(\rho_r - \rho_a)^2} \quad (4a)$$

The expression can be simplified because $\rho_r - \rho_a = (8006 - 1) \text{ kg m}^{-3} = 8005 \text{ kg m}^{-3} \approx 8006 \text{ kg m}^{-3}$:

$$\begin{aligned} \frac{\partial w_o}{\partial \rho_a} &= m_o \frac{8006(\rho_o - \rho_r)}{\rho_o \cdot 8006^2} \\ &= 1.25 \cdot 10^{-4} m_o \frac{\rho_o - 8006}{\rho_o} (\text{m}^3) \end{aligned} \quad (4b)$$

The individual influences of the parameters pressure, temperature, and humidity on the weight value can be

described by the relationship:

$$\frac{\partial w_o}{\partial \text{parameter}} = \frac{\partial w_o}{\partial \rho_a} \cdot \frac{\partial \rho_a}{\partial \text{parameter}} \quad (5)$$

The first factor is presented in Eq. (4b) whereas the second one is represented by the partial derivatives of Eq. (3):

$$\frac{\partial \rho_a}{\partial p} = \frac{A}{273.15 + t} (\text{kg m}^{-3} \text{ Pa}^{-1}) \quad \text{or} \quad (\text{s}^{-2} \text{ m}^{-2}) \quad (6a)$$

$$\frac{\partial \rho_a}{\partial t} = - \frac{(273.15 + t) \cdot B \cdot C \cdot h_r \cdot \exp(C \cdot t) + A \cdot p - B \cdot h_r \cdot \exp(C \cdot t)}{(273.15 + t)^2} (\text{kg m}^{-3} ^{\circ}\text{C}^{-1}) \quad (6b)$$

$$\frac{\partial \rho_a}{\partial h_r} = - \frac{B \cdot \exp(C \cdot t)}{273.15 + t} (\text{kg m}^{-3} \%^{-1}) \quad (6c)$$

Note that the slope of the pressure dependence is positive whereas it is negative for the influences of temperature and humidity. These relationships can also be found in our previous paper [5]. However, $\partial w_o/\partial \rho_a$ (Eqs. 4) is negative for weighing objects with $\rho_o < \rho_r$, therefore $\partial w_o/\partial p$ is negative for, e.g., aqueous samples and light metals whereas $\partial w_o/\partial t$ and $\partial w_o/\partial h_r$ are positive.

It was our goal to prove experimentally the relationships stated by the three possible Eq. (5). The validity of the function $\partial w_o/\partial p$ has already been shown with a weighing experiment of glass bottles in a laboratory with air conditioning, i.e. under constant temperature and humidity, therefore the pressure being the only influence parameter [5]. Now we investigated the relationships between weighing value and climate with objects from magnesium and aluminium in a room without air conditioning.

Experimental

Weighing Objects

We decided to perform this study with objects of low density and low specific surface but made from solid material (evacuated glass objects have very low mean density but they are too delicate for a long-term experiment). The air buoyancy effect is the more distinct the lower the density is, so we chose magnesium and aluminium objects. A small specific surface is necessary in order to keep the possible surface adsorption effects as low as possible. The best practical shape is a cylinder with equal diameter and height.

The objects of study were two nickel-plated magnesium cylinders and three anticorodal cylinders. The nickel plating of the magnesium pieces was necessary to prevent oxidation. Anticorodals are aluminium alloys with silicon, a small amount of

magnesium and traces of other elements. The masses of all cylinders were determined with highest care in a class E2 weighing laboratory at EMPA St. Gallen by considering the actual climate data.

The magnesium pieces had masses of approx. 77 g and 107 g (Mg 77 and Mg 107 in Table 2) and densities of 1829 kg m^{-3} and 1816 kg m^{-3} , respectively. The densities were calculated from the geometrical shapes of the cylinders with rounded

Table 1. Dates of weighings, weighing values in the order of experiments, and climate data. The weighing times are omitted for better clarity. The standard deviations of the weighing values are also noted at the end of the Table

| Date 2003 | Anticor 101 (g) | Anticor 6 (g) | Steel (g) | Anticor 69 (g) | Mg 77 (g) | Mg 107 (g) | p (hPa) | t (°C) | h_r (%) |
|---------------|-----------------|---------------|-----------|----------------|-----------|------------|-----------|----------|-----------|
| 9/16 | 101.0324 | 6.02467 | 49.99988 | 69.41448 | 77.16556 | 106.9168 | 977.444 | 23.610 | 47.16 |
| 9/17 | 101.0325 | 6.02470 | 49.99994 | 69.41455 | 77.16566 | 106.9170 | 976.188 | 23.843 | 50.22 |
| 9/18 | 101.0325 | 6.02462 | 49.99982 | 69.41452 | 77.16570 | 106.9171 | 973.340 | 24.670 | 47.27 |
| 9/23 | 101.0326 | 6.02454 | 49.99970 | 69.41451 | 77.16580 | 106.9174 | 967.214 | 24.943 | 50.45 |
| 9/25 | 101.0323 | 6.02464 | 49.99986 | 69.41437 | 77.16542 | 106.9167 | 979.706 | 24.574 | 45.10 |
| 9/26 | 101.0326 | 6.02468 | 49.99991 | 69.41459 | 77.16572 | 106.9171 | 974.692 | 24.501 | 42.37 |
| 9/27 | 101.0325 | 6.02468 | 49.99991 | 69.41461 | 77.16577 | 106.9171 | 971.154 | 24.125 | 44.34 |
| 10/1 | 101.0328 | 6.02470 | 49.99993 | 69.41474 | 77.16598 | 106.9175 | 962.813 | 22.938 | 44.85 |
| 10/3 | 101.0326 | 6.02471 | 49.99995 | 69.41468 | 77.16580 | 106.9171 | 966.695 | 21.854 | 56.58 |
| 10/8 | 101.0320 | 6.02465 | 49.99975 | 69.41423 | 77.16521 | 106.9163 | 970.750 | 21.597 | 44.58 |
| 10/9 | 101.0324 | 6.02467 | 49.99995 | 69.41441 | 77.16538 | 106.9166 | 971.953 | 21.173 | 46.22 |
| 10/13 | 101.0322 | 6.02468 | 49.99991 | 69.41436 | 77.16525 | 106.9164 | 974.018 | 21.006 | 49.51 |
| 10/15 | 101.0327 | 6.02468 | 50.00012 | 69.41467 | 77.16560 | 106.9169 | 975.089 | 21.965 | 42.12 |
| 10/18 | 101.0324 | 6.02463 | 49.99986 | 69.41447 | 77.16554 | 106.9169 | 965.754 | 21.559 | 40.83 |
| 10/20 | 101.0329 | 6.02464 | 49.99983 | 69.41480 | 77.16617 | 106.9178 | 951.248 | 22.400 | 46.46 |
| 10/21 | 101.0325 | 6.02469 | 49.99981 | 69.41457 | 77.16575 | 106.9172 | 960.231 | 22.097 | 46.52 |
| 10/24 | 101.0325 | 6.02465 | 49.99984 | 69.41463 | 77.16570 | 106.9170 | 968.441 | 23.027 | 41.01 |
| 10/25 | 101.0324 | 6.02466 | 49.99989 | 69.41450 | 77.16546 | 106.9168 | 973.058 | 23.119 | 35.93 |
| 10/27 | 101.0324 | 6.02467 | 49.99988 | 69.41451 | 77.16553 | 106.9169 | 969.324 | 22.954 | 36.27 |
| 10/28 | 101.0325 | 6.02462 | 49.99986 | 69.41452 | 77.16557 | 106.9169 | 968.305 | 22.784 | 35.76 |
| 10/29 | 101.0328 | 6.02469 | 49.99985 | 69.41480 | 77.16611 | 106.9176 | 954.105 | 22.926 | 37.34 |
| 10/31 | 101.0334 | 6.02469 | 49.99987 | 69.41515 | 77.16679 | 106.9187 | 936.720 | 22.617 | 34.24 |
| 11/3 | 101.0321 | 6.02467 | 49.99983 | 69.41433 | 77.16522 | 106.9164 | 974.304 | 21.849 | 46.80 |
| 11/4 | 101.0321 | 6.02463 | 49.99986 | 69.41424 | 77.16502 | 106.9162 | 982.407 | 22.502 | 46.20 |
| 11/6 | 101.0322 | 6.02463 | 49.99988 | 69.41433 | 77.16520 | 106.9164 | 979.753 | 23.049 | 42.84 |
| 11/7 | 101.0323 | 6.02464 | 49.99989 | 69.41439 | 77.16533 | 106.9166 | 974.960 | 22.117 | 37.53 |
| 11/9 | 101.0321 | 6.02468 | 49.99987 | 69.41434 | 77.16519 | 106.9164 | 976.578 | 22.300 | 38.17 |
| 11/10 | 101.0323 | 6.02461 | 49.99987 | 69.41440 | 77.16535 | 106.9166 | 974.018 | 22.591 | 41.65 |
| 11/12 | 101.0322 | 6.02465 | 49.99982 | 69.41438 | 77.16533 | 106.9165 | 973.174 | 22.550 | 39.35 |
| 11/13 | 101.0322 | 6.02470 | 49.99993 | 69.41438 | 77.16525 | 106.9165 | 979.653 | 22.820 | 46.45 |
| 11/14 | 101.0323 | 6.02466 | 49.99987 | 69.41442 | 77.16532 | 106.9166 | 973.192 | 22.124 | 46.43 |
| 11/16 | 101.0323 | 6.02465 | 49.99988 | 69.41445 | 77.16542 | 106.9167 | 966.713 | 20.833 | 38.81 |
| 11/17 | 101.0321 | 6.02469 | 49.99992 | 69.41432 | 77.16512 | 106.9163 | 978.745 | 21.473 | 41.62 |
| 11/18 | 101.0322 | 6.02467 | 49.99994 | 69.41435 | 77.16513 | 106.9163 | 979.483 | 22.124 | 46.02 |
| 11/19 | 101.0322 | 6.02462 | 49.99985 | 69.41430 | 77.16515 | 106.9164 | 976.375 | 21.568 | 44.37 |
| 11/20 | 101.0323 | 6.02463 | 49.99984 | 69.41439 | 77.16532 | 106.9165 | 971.613 | 21.646 | 41.63 |
| 11/21 | 101.0325 | 6.02469 | 49.99996 | 69.41461 | 77.16559 | 106.9170 | 968.193 | 22.169 | 41.89 |
| 11/23 | 101.0326 | 6.02469 | 49.99989 | 69.41462 | 77.16571 | 106.9171 | 959.608 | 21.336 | 40.66 |
| 11/24 | 101.0326 | 6.02470 | 49.99989 | 69.41466 | 77.16582 | 106.9173 | 959.237 | 21.721 | 45.25 |
| 11/25 | 101.0325 | 6.02467 | 49.99987 | 69.41454 | 77.16562 | 106.9170 | 963.054 | 21.060 | 45.37 |
| 11/26 | 101.0328 | 6.02468 | 49.99988 | 69.41477 | 77.16601 | 106.9176 | 954.837 | 21.695 | 46.47 |
| 11/27 | 101.0328 | 6.02471 | 49.99986 | 69.41479 | 77.16611 | 106.9176 | 951.990 | 22.537 | 40.89 |
| 12/2 | 101.0324 | 6.02465 | 49.99982 | 69.41447 | 77.16555 | 106.9169 | 964.016 | 22.075 | 41.69 |
| 12/3 | 101.0324 | 6.02463 | 49.99983 | 69.41445 | 77.16545 | 106.9168 | 969.167 | 22.096 | 42.02 |
| 12/4 | 101.0323 | 6.02465 | 49.99987 | 69.41441 | 77.16538 | 106.9166 | 971.903 | 22.457 | 43.96 |
| 12/5 | 101.0322 | 6.02462 | 49.99986 | 69.41429 | 77.16514 | 106.9163 | 977.382 | 21.985 | 40.74 |
| 12/8 | 101.0321 | 6.02465 | 49.99990 | 69.41433 | 77.16518 | 106.9163 | 976.131 | 21.508 | 34.59 |
| 12/10 | 101.0323 | 6.02463 | 49.99981 | 69.41444 | 77.16550 | 106.9167 | 967.468 | 22.063 | 34.62 |
| 12/12 | 101.0322 | 6.02465 | 49.99987 | 69.41439 | 77.16530 | 106.9165 | 976.247 | 22.705 | 41.79 |
| 12/15 | 101.0323 | 6.02470 | 49.99989 | 69.41439 | 77.16534 | 106.9166 | 971.993 | 21.804 | 38.80 |
| 12/19 | 101.0322 | 6.02467 | 49.99989 | 69.41440 | 77.16534 | 106.9165 | 974.415 | 22.443 | 41.03 |
| 12/23 | 101.0318 | 6.02461 | 49.99973 | 69.41398 | 77.16463 | 106.9156 | 980.640 | 20.708 | 30.75 |
| St. dev. (mg) | 0.27 | 0.033 | 0.062 | 0.19 | 0.35 | 0.50 | | | |
| RSD (ppm) | 2.7 | 5.4 | 1.2 | 2.7 | 4.6 | 4.7 | | | |

edges. The density difference stems from the different nickel coatings.

The anticorodal pieces had masses of approx. 6 g, 69 g and 101 g (AC 6, AC 69 and AC 101 in Table 2). Their density was 2752 kg m^{-3} as determined by the immersion method.

Acquisition of the Climate Data

The data of air pressure, temperature and humidity were automatically registered every 10 minutes during the whole period of the weighing experiment (from Sept. 16 to Dec. 23, 2003). The instrument was a Klimet A30 (Meteolabor AG, CH-8620 Wetzikon, Switzerland, www.meteolabor.ch). All data are means of 10 consecutive measurements during 70 seconds. The resolutions are 0.1 Pa, 0.001 °C and 0.01%, the accuracies are $\pm 4 \text{ Pa}$, $\pm 0.05 \text{ °C}$ and $\pm 0.15\%$, respectively (data from the technical description sheet of the instrument). The sensors were mounted sidewise and in close proximity to the balance.

There were some interruptions of the data acquisition process during the time of the experiment but we got almost 11,800 climate data sets. They are discussed in the Climate Behaviour section below. The air densities at the moment of weighings were calculated from these data by using Eq. (3).

Weighing Experiments

The weighings were performed at the Kantonsschule (grammar school) of Heerbrugg in a lecture preparation room without air conditioning. The operators were instructed to weigh the magnesium and anticorodal cylinders once a day if they could take their time for this extra duty. They did not do any mass calculations, so they did not control the quality of their measurements. The weighing objects were handled with tweezers and stored in soft paper, cardboard box and a nearby drawer.

52 weighing series could be performed between Sept. 16 and Dec. 23, 2003. A steel cylinder with density 8006 kg m^{-3} and a mass of 49.99985 g was also weighed. Its results were used for the correction of the other data: Because its density is equal to the one of the built-in reference weight, its weight value is equal to its mass and should not depend on climatic conditions. In fact, we observed random deviations of $\pm 0.2 \text{ mg}$ (extreme values) or a standard deviation of 0.06 mg. These deviations were looked at as linear offsets of the balance at the moment of the weighing and were added or subtracted to the weighing values of the magnesium and anticorodal pieces.

The balance was a Mettler Toledo AX 205 DR (Mettler Toledo, Greifensee, Switzerland, www.mt.com) with a readability of 0.01 mg from 0 to 81 g and of 0.1 mg in the upper range to 220 g. The balance was calibrated by DKD (Deutscher Kalibrierdienst, Giessen, Germany) on June 11, 2003. The calibration certificate states the following expanded uncertainties U (95%):

- Lower range: $U = 0.029 \text{ mg} + 7.0 \cdot 10^{-6} \cdot \text{load (in mg)}$
- Upper range: $U = 0.00060 \text{ g} + 4.6 \cdot 10^{-6} \cdot \text{load (in g)}$

These data give the uncertainties u ($= 0.5 U$):

- for 6 g: 0.0355 mg or 5.9 ppm
- for 69 g: 0.26 mg or 3.7 ppm
- for 77 g: 0.28 mg or 3.7 ppm
- for 101 g: 0.53 mg or 5.3 ppm
- for 107 g: 0.55 mg or 5.1 ppm

The weighing uncertainty according to the Reichmuth et al. paper [2] and the technical balance data of Mettler Toledo is 2.9 ppm

for all pieces with the exception of the 6 g anticorodal cylinder whose uncertainty is 3.4 ppm (0.021 mg). The difference of the two approaches comes from their diverse concepts (above all the consideration of eccentric load in the DKD certificate and the fact that the repeatability was determined with the given balance and not taken from experience).

The climate data were stored automatically whenever a series of weighings was performed.

All weighing data and the related climate data are presented in Table 1.

Results and Discussion

Data Treatment

The experimental weighing values depend on the three parameters pressure, temperature and relative humidity. If the sole influence of one of them is to be demonstrated it is necessary to calculate hypothetical weighing values by holding this parameter constant while the other two ones vary in the same way as they did during the experiment. It is obvious that the mean values of the parameters are selected as constants:

- mean pressure at the time of the 52 weighing experiments = 96991.3 Pa
- mean temperature = 22.388 °C
- mean relative humidity = 42.57%

The experimental slopes are obtained from the linear relationships between the hypothetical weighing values and the parameter in question.

Example: the influence of temperature on the weighing values of Mg 77. The first experiment (Sept. 16, see Table 1) gave a weighing value of 77.16556 g. The steel reference weight was 49.99988 g, i.e. 0.03 mg higher than its conventional true value. Therefore the corrected weighing value of Mg 77 was 0.03 mg lower than the balance reading, namely 77.16553 g. Now a virtual air density was calculated with Eq. (3) and the following data: actual pressure = 97744.4 Pa, actual relative humidity = 47.16%, and mean temperature = 22.388 °C, giving $\rho_a = 1.14694 \text{ kg m}^{-3}$. This value was used in mass Eq. (1) for the calculation of a virtual weighing value of Mg 77 at the mean temperature. The result is 77.20574 g. In Fig. 2 it is assigned to its real temperature of 23.610 °C.

By doing so for all 52 experimental data, one gets a series of virtual weighing values which yields a linear relationship when plotted against the actual temperatures pertinent to the respective experiments. The slope of this function should be equal to the theoret-

ical value calculated by Eq. (5); this equation needs data obtained by Eqs. (4) and (6). The masses m_o , needed in Eq. (4), are the ones determined in the EMPA laboratory, see Table 2. For the partial derivatives of Eqs. (6a) to (6c) again the above-mentioned means of pressure, temperature and humidity were used, giving the following values:

$$\begin{aligned}\partial\rho_a/\partial p &= 1.179 \cdot 10^{-5} \text{ kg m}^{-3} \text{ Pa}^{-1} \\ \partial\rho_a/\partial t &= -4.166 \cdot 10^{-5} \text{ kg m}^{-3} \text{ }^\circ\text{C}^{-1} \\ \partial\rho_a/\partial h_r &= -1.202 \cdot 10^{-4} \text{ kg m}^{-3} \text{ } \%\text{ }^{-1}\end{aligned}$$

Comparison of Theoretical and Experimental Slopes

All virtual weighing values, obtained as described above, are shown in Fig. 1 (pressure dependence),

Fig. 2 (temperature dependence), and Fig. 3 (humidity dependence). The Figs. are not in SI units but the weighing values are in g and the pressure is in hPa. Table 2 presents the theoretical and experimental slopes $\partial w_o/\partial p$, $\partial w_o/\partial t$ and $\partial w_o/\partial h_r$ for the five test cylinders.

The AC 6 data (in the upper right of Figs. 1–3) show large scattering. In addition, they all include an outlier, namely the measurement of Oct. 15. (The other cylinders do not show extraordinary values on this day.) The outliers were rejected for the calculation of the slopes, but even then the correlation coefficients for AC 6 are poor or even inexistent, see Table 2. Surprisingly enough, the match between the theoretical slopes is good for the influences of pressure and temperature but the one for the humidity influence is off. The possible effect is too low to be observed with a 6 g object.

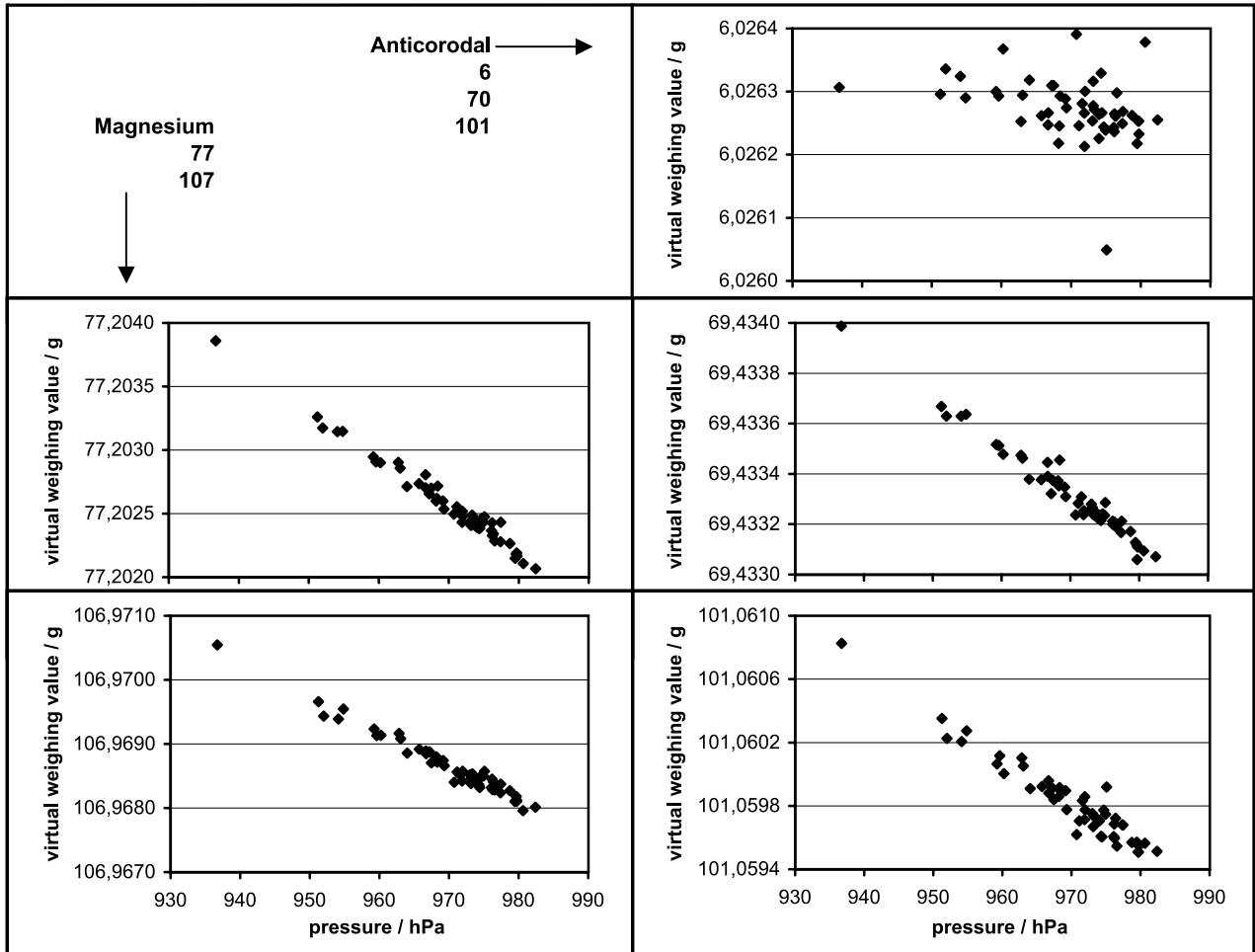


Fig. 1. Dependence of the virtual weighing values of the five test cylinders from the atmospheric pressure

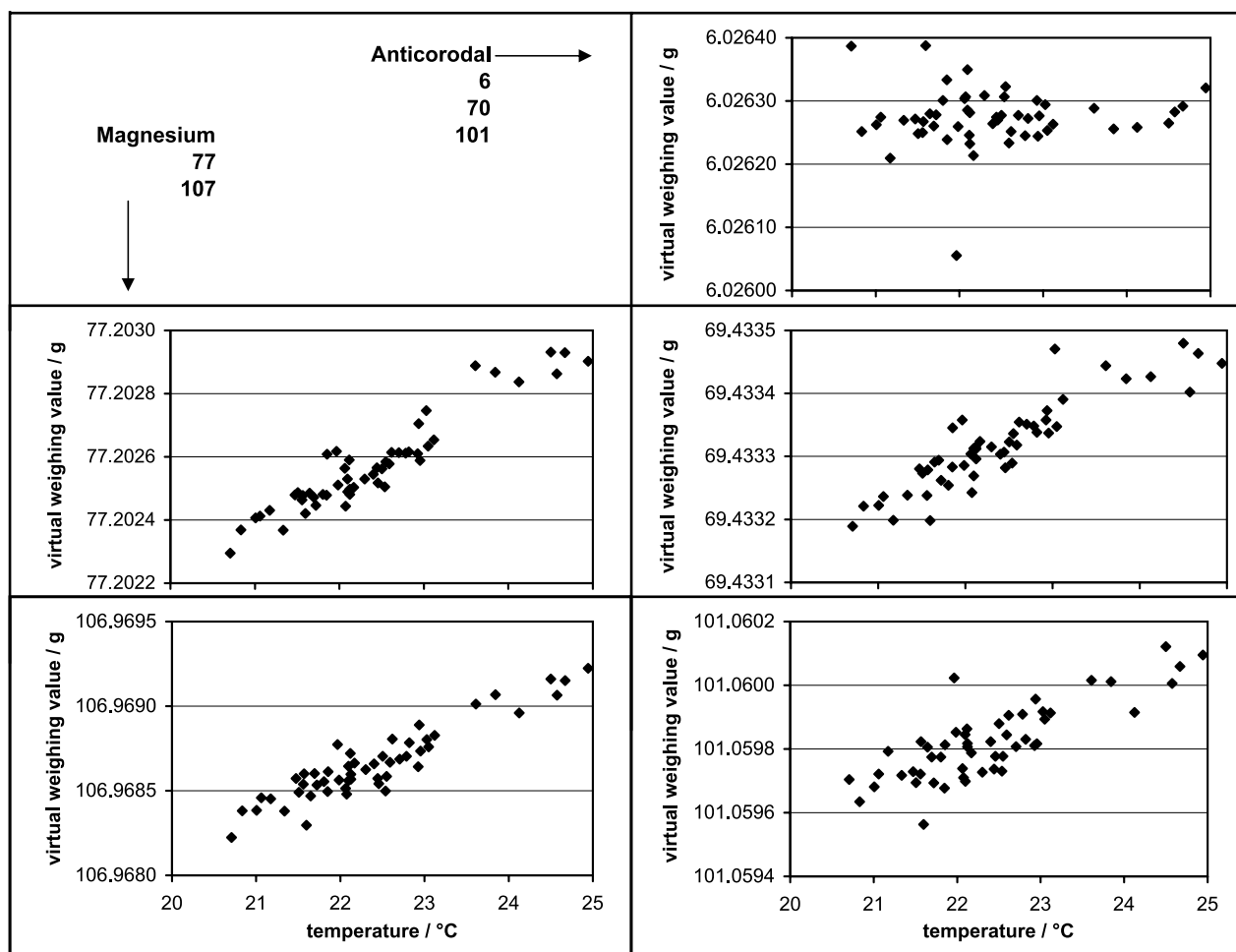


Fig. 2. Dependence of the virtual weighing values of the five test cylinders from the temperature

With the other four pieces the effect of pressure is distinct and the match between theoretical and experimental slopes is excellent. The effect of temperature is weaker but the match of slopes is again almost perfect thanks to the large number of data points. With regard to humidity the correlations are weak but the slopes are of the correct order of magnitude. It is possible that water adsorption effects interfere with the influence of air density on the weighing value; however, the experimental slopes do not show a uniform behaviour. Three of them are too high but one (AC 69) is too low. Water adsorption layers on steel have been investigated by Schwartz [6]. It was found that their thickness correlates with the relative humidity of the surrounding air; however, it is not straightforward to draw any conclusions for the present study.

Climate Behaviour and Measurement Uncertainty

The masses of the cylinders could be determined with a long-term relative repeatability of less than 1 ppm (Table 2) with the exception of the 6 g anticorodal piece. Such excellent repeatabilities, much better than the uncertainty of the balance data, are not representative for common weighing tasks. They do not include the inherent uncertainty of the balance in question, namely its nonlinearity, sensitivity tolerance, and temperature coefficient. In addition, the masses are not weighing values but they are corrected by the effect of air buoyancy; a correction usually not made for common chemical analyses. Another correction was the additive one performed with the weighing value obtained for the steel cylinder.

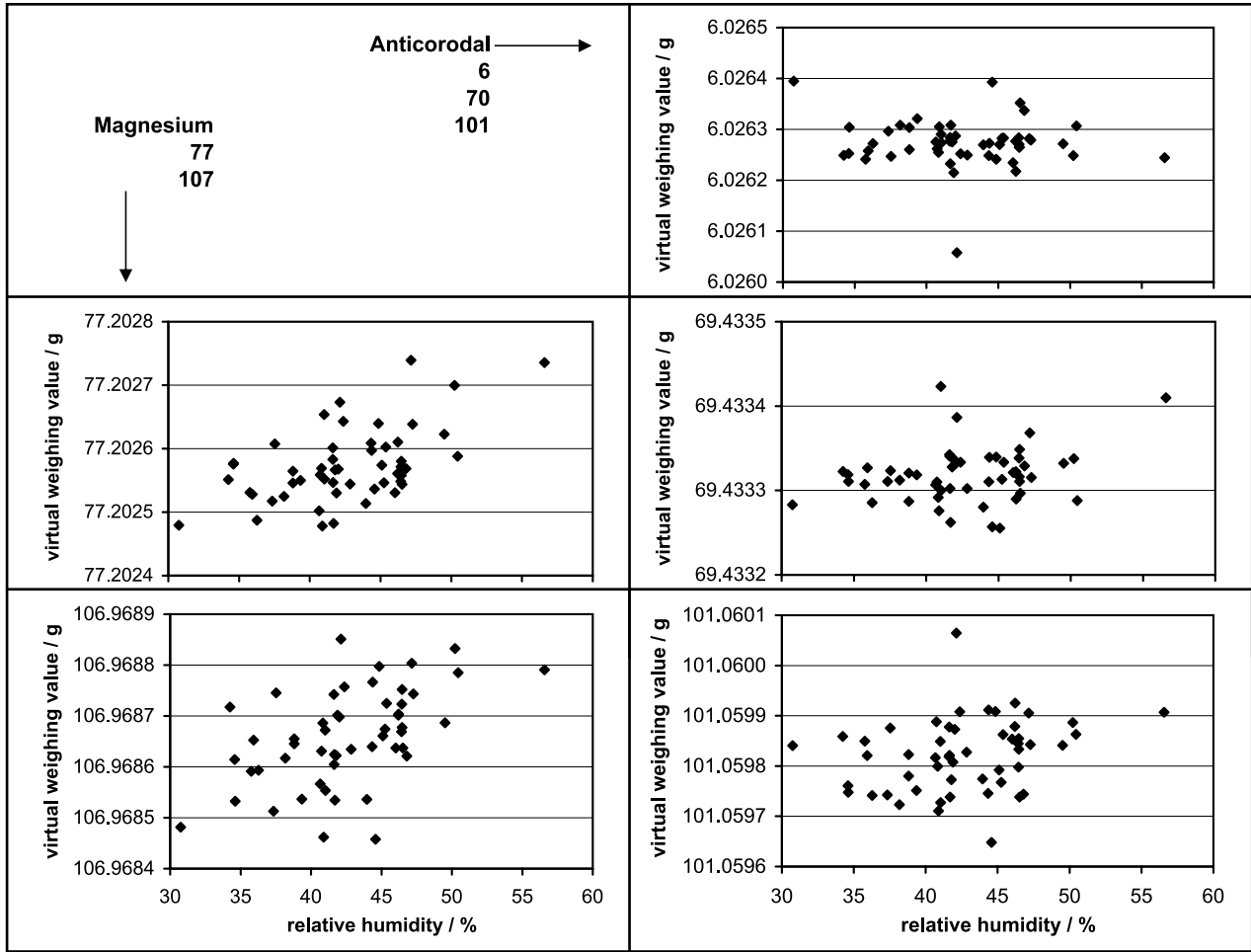


Fig. 3. Dependence of the virtual weighing values of the five test cylinders from the relative humidity

Table 2. Conventional true masses, theoretical slopes, experimental slopes, and experimental mass standard deviations of the test cylinders (different order than in Table 1). In the AC 6 data set the outliers of Oct. 15 were not considered

| Property | Equations | Mg 77 | Mg 107 | AC 6 | AC 69 | AC 101 |
|--|-----------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Mass (kg) | 1 | 0.0772025 | 0.10697 | 0.0060263 | 0.069433 | 0.10106 |
| $\partial w_o / \partial \rho_a$ (m ³) | 4a | $-3.26 \cdot 10^{-5}$ | $-4.56 \cdot 10^{-5}$ | $-1.44 \cdot 10^{-6}$ | $-1.66 \cdot 10^{-5}$ | $-2.41 \cdot 10^{-5}$ |
| $\partial w_o / \partial p$ th. (kg Pa ⁻¹) | 5, 6a | $-3.84 \cdot 10^{-10}$ | $-5.37 \cdot 10^{-10}$ | $-1.70 \cdot 10^{-11}$ | $-1.95 \cdot 10^{-10}$ | $-2.84 \cdot 10^{-10}$ |
| $\partial w_o / \partial p$ exp. (kg Pa ⁻¹) | | $-3.73 \cdot 10^{-10}$ | $-5.30 \cdot 10^{-10}$ | $-1.68 \cdot 10^{-11}$ | $-1.95 \cdot 10^{-10}$ | $-2.74 \cdot 10^{-10}$ |
| Correlation coefficient r | | -0.99 | -0.985 | -0.38 | -0.98 | -0.96 |
| $\partial w_o / \partial t$ th. (kg °C ⁻¹) | 5, 6b | $1.36 \cdot 10^{-7}$ | $1.90 \cdot 10^{-7}$ | $5.99 \cdot 10^{-9}$ | $6.90 \cdot 10^{-8}$ | $1.00 \cdot 10^{-7}$ |
| $\partial w_o / \partial t$ exp. (kg °C ⁻¹) | | $1.47 \cdot 10^{-7}$ | $2.08 \cdot 10^{-7}$ | $6.99 \cdot 10^{-9}$ | $6.58 \cdot 10^{-8}$ | $1.00 \cdot 10^{-7}$ |
| Correlation coefficient r | | 0.95 | 0.93 | -0.02 | 0.90 | 0.82 |
| $\partial w_o / \partial h_r$ th. (kg % ⁻¹) | 5, 6c | $3.92 \cdot 10^{-9}$ | $5.47 \cdot 10^{-9}$ | $1.73 \cdot 10^{-10}$ | $1.99 \cdot 10^{-9}$ | $2.90 \cdot 10^{-9}$ |
| $\partial w_o / \partial h_r$ exp. (kg % ⁻¹) | | $6.57 \cdot 10^{-9}$ | $9.97 \cdot 10^{-9}$ | $-1.07 \cdot 10^{-9}$ | $1.78 \cdot 10^{-9}$ | $3.82 \cdot 10^{-9}$ |
| Correlation coefficient r | | 0.54 | 0.51 | -0.14 | 0.26 | 0.26 |
| Exp. mass stand. dev. (mg) | | 0.059 | 0.083 | 0.037 | 0.031 | 0.069 |
| Exp. RSD (ppm) | | 0.77 | 0.78 | 6.1 | 0.45 | 0.69 |

The climate data, a total of 11,800 data sets, can be classified in histograms (Fig. 4). We assume that they are not really representative for a full year; the summer

months were missing in our study, and they usually bring higher temperatures and humidities. Nevertheless, for uncertainty determinations the behaviour of

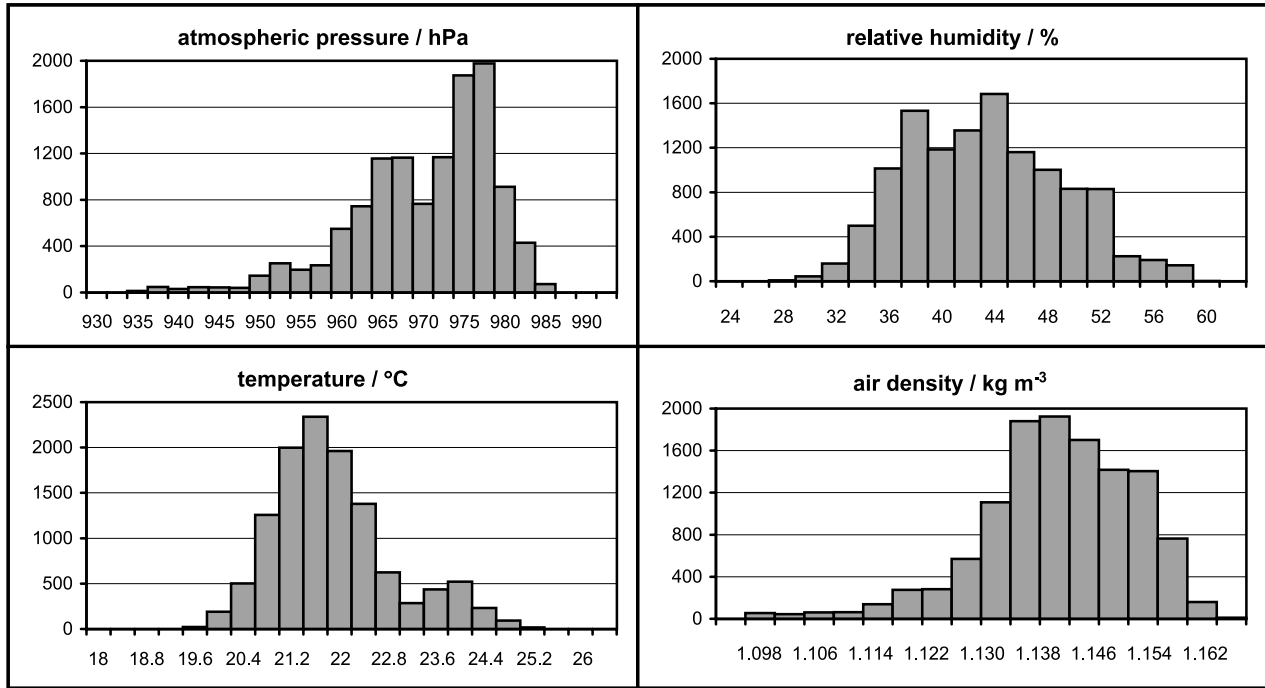


Fig. 4. Distribution of the climate parameters at Heerbrugg in the period from Sept. 16 to Dec. 23, 2003. Pressure, temperature and humidity represent measured data whereas the air densities were calculated from these parameters

pressure, temperature, humidity, and air density can be looked at as triangularly distributed (as a reasonable approximation). This finding is in contrast to our previous proposal. We wrote [2]:

“For the uncertainty of the air density it is convenient to calculate the extreme values which may occur in the laboratory and to treat these data as the boundaries of a rectangular distribution. The extremes are the combination of high atmospheric pressure, low temperature and low humidity on the one hand, and low pressure, high temperature and high humidity on the other.”

Such an approach is too conservative. The extremes of the 11,800 values were as follows:

- pressure: from 934 to 984 hPa
- temperature: from 18.1 to 25.1 °C
- humidity: from 27 to 58%

These data give calculated extreme air densities of 1.083 and 1.174 kg m⁻³. The uncertainty of air density is 0.026 kg m⁻³ or 2.3% when treated as a rectangular distribution [1] ($\Delta \text{density}/2\cdot\sqrt{3}$). But if we assume a triangular distribution, the uncertainty is lower, namely 0.019 kg m⁻³ or 1.7% ($\Delta \text{density}/2\cdot\sqrt{6}$).

Even this latter calculation does not represent the reality. It is not reasonable to assume that the

extremes of the three climate parameters occur at the same time. In fact, the extreme air densities of our 11,800 data sets were 1.099 and 1.163 kg m⁻³. We obtain an uncertainty of the air density of 0.013 kg m⁻³ or 1.15% with the triangular approach.

The only correct approach for the uncertainty of air density is given by the following equation [1]:

$$u_c(\rho_a) = \rho_a \sqrt{\left(\frac{\partial \rho_a}{\partial p}\right)^2 u^2(p) + \left(\frac{\partial \rho_a}{\partial t}\right)^2 u^2(t) + \left(\frac{\partial \rho_a}{\partial h_r}\right)^2 u^2(h_r)} \quad (7)$$

The partial derivatives are noted in Eqs. (6a) to (6c). The uncertainties $u(p)$, $u(t)$ and $u(h_r)$ are obtained from our climate data by treating the extreme values as the boundaries of triangular distributions, giving $u(p) = 1015 \text{ Pa}$, $u(t) = 1.43 \text{ °C}$ and $u(h_r) = 6.33\%$. Then we get an uncertainty of air density of 0.015 kg m⁻³ or 1.3%.

Therefore we can revise our statement and propose to use the model of Eq. (7) with triangularly distributed climate parameters. But we must not forget that it is not the uncertainty of the air density which dominates the uncertainty of many weighing operations but the uncertainty of the density of the weighing object [2].

Conclusions

Weighing values reflect climate conditions to an extent which can easily be observed. For mass determinations with an accuracy of approx. 10^{-3} (depending on the density of the weighing object) it is necessary to correct the weight value by the buoyancy factor. An air-conditioned weighing laboratory is to be preferred although it only eliminates the influences of temperature and humidity but not the one of atmospheric pressure; this latter effect is the most prominent one.

The step from weighing values to masses reduces the long-term relative standard deviation from typically 2–5 ppm to less than 1 ppm, see the bottom lines of Tables 1 and 2. (AC 6 is an exception because the mass of this cylinder is almost too low for our type of experiment. In Table 1 the Steel results are also an exception because they do not depend on the climate conditions.)

The uncertainty of the air density, which needs to be known for the uncertainty calculation of masses, is best determined in the metrologically correct way by using Eq. (7). If $u(t)$ and $u(h_r)$ are small compared to $u(p)$ because the balance is in an air-conditioned room, then the relationship simplifies to:

$$u(\rho_a) = \rho_a \left(\frac{\partial \rho_a}{\partial p} \right) u(p) \quad (8a)$$

or with the partial derivative presented in Eq. (6a) and a triangular distribution of the pressure:

$$u(\rho_a) = \rho_a \frac{0.0034848}{273.15 + t} \cdot \frac{p_{\max} - p_{\min}}{2 \cdot \sqrt{6}} \quad (8b)$$

Our previous paper [2] discussed how the measurement uncertainty $u(\text{mass})$ is calculated. Besides the uncertainty of the air density $u(\rho_a)$, also the uncertainties of the weighing value $u(w_o)$, of the reference weight density $u(\rho_r)$ and of the object density $u(\rho_o)$ need to be known. The last parameter can be the most

uncertain one whereas $u(\rho_r)$ usually is 10 kg m^{-3} . $u(w_o)$ depends on the technical parameters of the balance. The relative combined standard uncertainty of a mass determination with an electronic laboratory balance is then, in accordance to Eq. (1):

$$\frac{u_c(m_o)}{m_o} = \sqrt{\left(\frac{u(w_o)}{w_o} \right)^2 + \left(\frac{\rho_o}{\rho_r(\rho_o - \rho_a)} \right)^2 \cdot \left[\left(\frac{\rho_r \cdot \rho_a}{\rho_o(\rho_o - \rho_a)} \right)^2 u^2(\rho_o) + \left(\frac{\rho_a}{\rho_r} \right)^2 u^2(\rho_r) + \left(\frac{\rho_r - \rho_o}{\rho_o - \rho_a} \right)^2 u^2(\rho_a) \right]} \quad (9)$$

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